

THERMOELECTRIC BONDING STUDY

Covering the Period from  
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HITTMAN ASSOCIATES, INC.  
BALTIMORE, MARYLAND

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ABSTRACT

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Braze process development for n-PbTe has been completed and a bonding specification prepared. This process required modification, notably slow cooling, to be applied to p-PbTe. A fixture in which eight elements may be bonded simultaneously has been fabricated and employed in bonding p-PbTe thermoelements.

Most elements manufactured during the quarter were p-PbTe hot pressed from 3M Company TEG-2P powder. As-pressed Seebeck Coefficient and electrical resistivity were consistently about 10 percent below the published 3M values.

The use of additives to increase the strength of p-PbTe is under study. Preliminary results indicate that molybdenum is particularly effective and that tungsten and  $\text{Al}_2\text{O}_3$  fibers may also have value for this application.

A currently operating life test of n-PbTe has passed 2000 hours without degradation. Microprobe analysis of samples operated for 200 and 500 hours showed that extensive interdiffusion occurs between the braze and thermoelectric material. A 500 hour life test of p-PbTe thermoelements yielded inconclusive results. Longer term tests are underway.

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## I. INTRODUCTION

Hittman Associates, Inc., under Contract NAS5-3973, has been engaged in a program whose immediate objective has been to gain an understanding of the mechanisms by which bonds between lead telluride and metal shoes degrade and ultimately fail. Considerable progress has been made and is discussed in earlier reports in this series (see, for example, References 1 and 2).

An apparently satisfactory bond for n-PbTe has been developed and life tests to prove its reliability for long term operation are now underway. Work with p-PbTe includes strengthening of the elements to eliminate cracking during cooling from the bonding temperatures and braze process development. Progress in these areas is reported in the following sections.

## II. BRAZE PROCESS

### A. n-Type PbTe

The process for bonding n-PbTe to iron contacts with titanium modified tin telluride has progressed sufficiently that a tentative specification can be formulated. This process is divided into three steps - (1) preparation of the braze, (2) preparation of the element and shoe for bonding, and (3) the bonding operation itself. Each step is described below.

#### 1. Preparation of the Braze Material

The braze alloy consists of SnTe modified by the addition of one percent by weight of titanium metal. The alloy composition is approximately 46.2 w/o Sn - 52.8 w/o Te - 1 w/o Ti. Purity of the starting tin and tellurium is 99.999 while that of the titanium is 99 percent. The braze is prepared in twenty-five gram batches by weighing out the constituents to the nearest 0.01 gram and placing them in a clean vycor tube. The tube is then evacuated and backfilled with dried argon. This evacuation-filling operation is repeated at least ten times and the tube is finally filled with argon at one half atmosphere and sealed. The capsule is placed in a furnace at 1600°F and held for approximately one hour, being agitated periodically to assure alloying. The resultant melt is crushed and sifted through a -200 mesh screen and the powder is rebled to assure homogeneity. Braze wafers, approximately 3/8 inch diameter by 0.01 inch high, are pressed in a steel die at 45,000 psi. The wafers, separated by alundum sand, are sealed in a vycor capsule by a process identical with that described above for the alloy constituents. Sintering is carried out at 1000°F for one hour. The wafers are stored in an argon atmosphere until used.

#### 2. Preparation of the Element and Shoes

The present procedure is identical for preparing elements and shoes. The ends of the element or shoe are ground square in a vee block using 240 grit metallographic paper. The sample is then polished successively through 320, 400, and 600 grit papers and is finished on a billiard cloth polishing wheel with #3 universal diamond paste. The element or shoe is then cleaned with soap and water, rinsed with hot water, dried, wiped thoroughly with acetone twice, rinsed with methanol twice, and dried.

#### 3. Bonding Operation

The cleaned iron shoe, a braze wafer, and the thermoelectric element are placed in a graphite bonding die and this is, in turn, inserted into a stainless steel retaining fixture. Light pressure is applied by means of a spring. This apparatus is shown in Figure 1. The assembled bonding fixture is placed in a vycor type located in a furnace. The tube is evacuated and then backfilled with argon. A slight argon flow is maintained during bonding. The temperature is raised to 1500°F, held for five minutes, and allowed to cool to 1000 - 1100°F in the furnace. The assembly, still in the vycor tube, is then removed from the furnace and placed in a brick holding chamber in which it cools to about 400°F in thirty minutes. The bonded element may be removed from the fixture at or below



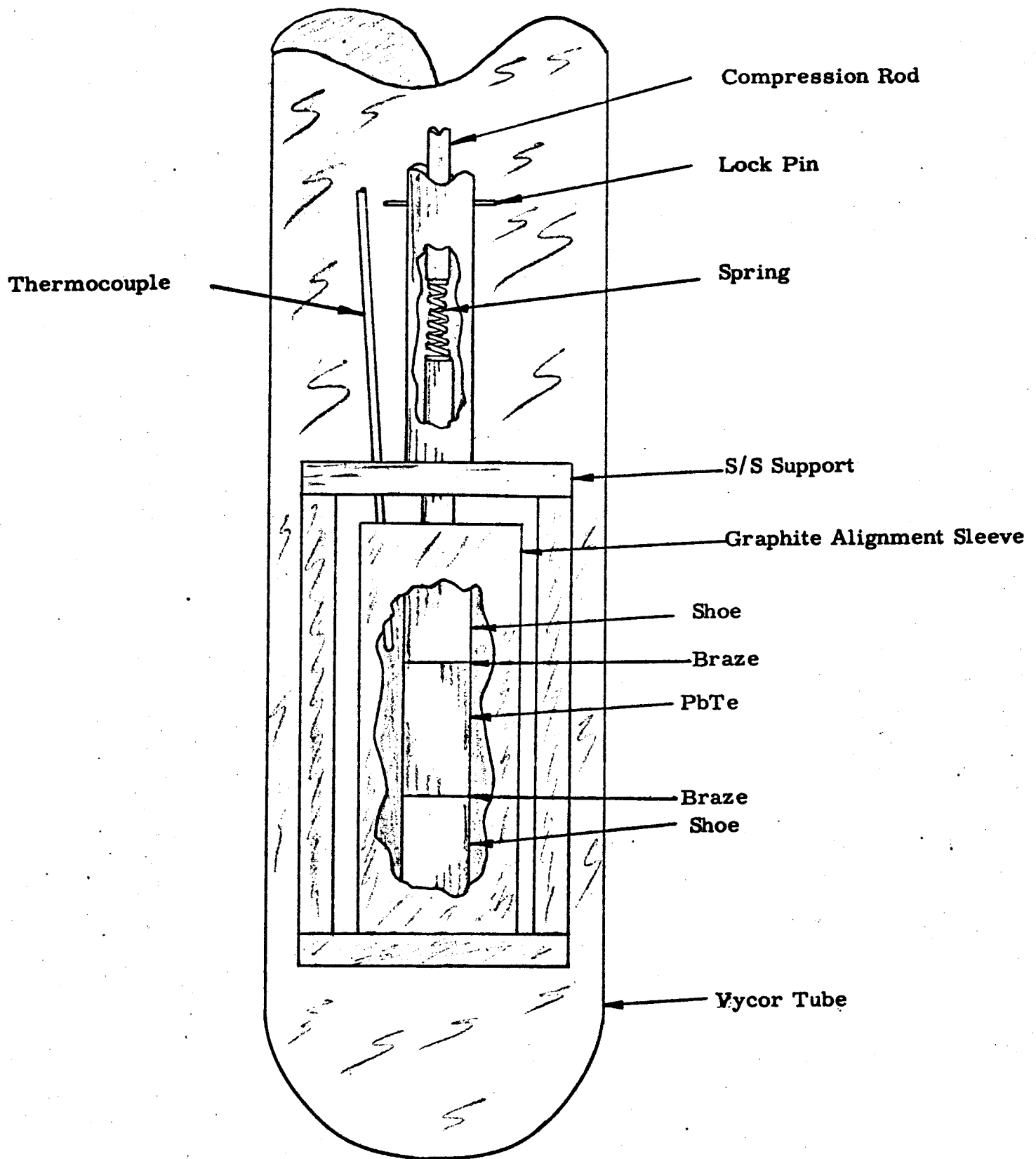


Figure 1. Bonding Fixture for n-PbTe Thermoelectric Elements

this temperature. Experimental variation of  $20^{\circ}\text{F}$  or so in the bonding temperature appears to have no effect on the results.

#### B. p-Type PbTe

An intensive investigation of TEG-2P p-PbTe during this quarter included study of the bonding of this material to iron shoes. The process described above proved to be unsatisfactory. The stresses generated during cooldown were sufficient to initiate cracks and most bonded elements fractured within the thermoelectric material during handling subsequent to bonding. Acceptable bonds were made by permitting the bonded element to slowly cool to room temperature in the furnace. This resulted in a three to four hour cooldown cycle and restricted daily production to a maximum of three elements.

To overcome this limitation, the multiple element bonding fixture depicted in Figure 2 was designed and built. The major differences between this device and that employed for n-PbTe are that up to eight elements are bonded simultaneously and the small compressive load is applied by steel weights rather than by spring loading. Because the diameter of the bonding fixture is greater than that of available vycor tubes, bonding is carried out in an argon atmosphere stainless steel pot furnace. The temperatures and holding time are similar to those used for n-PbTe, but sufficient numbers of bonds have not yet been made to fully determine the optimum parameters. Satisfactory bonds are being regularly produced in this device.

The same process is being used to bond p-PbTe elements containing additives which are being studied as part of this program and are described elsewhere in this report. No difficulty has been encountered in this work.

A number of torsion test samples of p-PbTe, with and without additions, have been bonded to iron shoes by the above described process. A special graphite fixture for multiple bonds similar to that shown in Figure 2 was used in making these specimens.

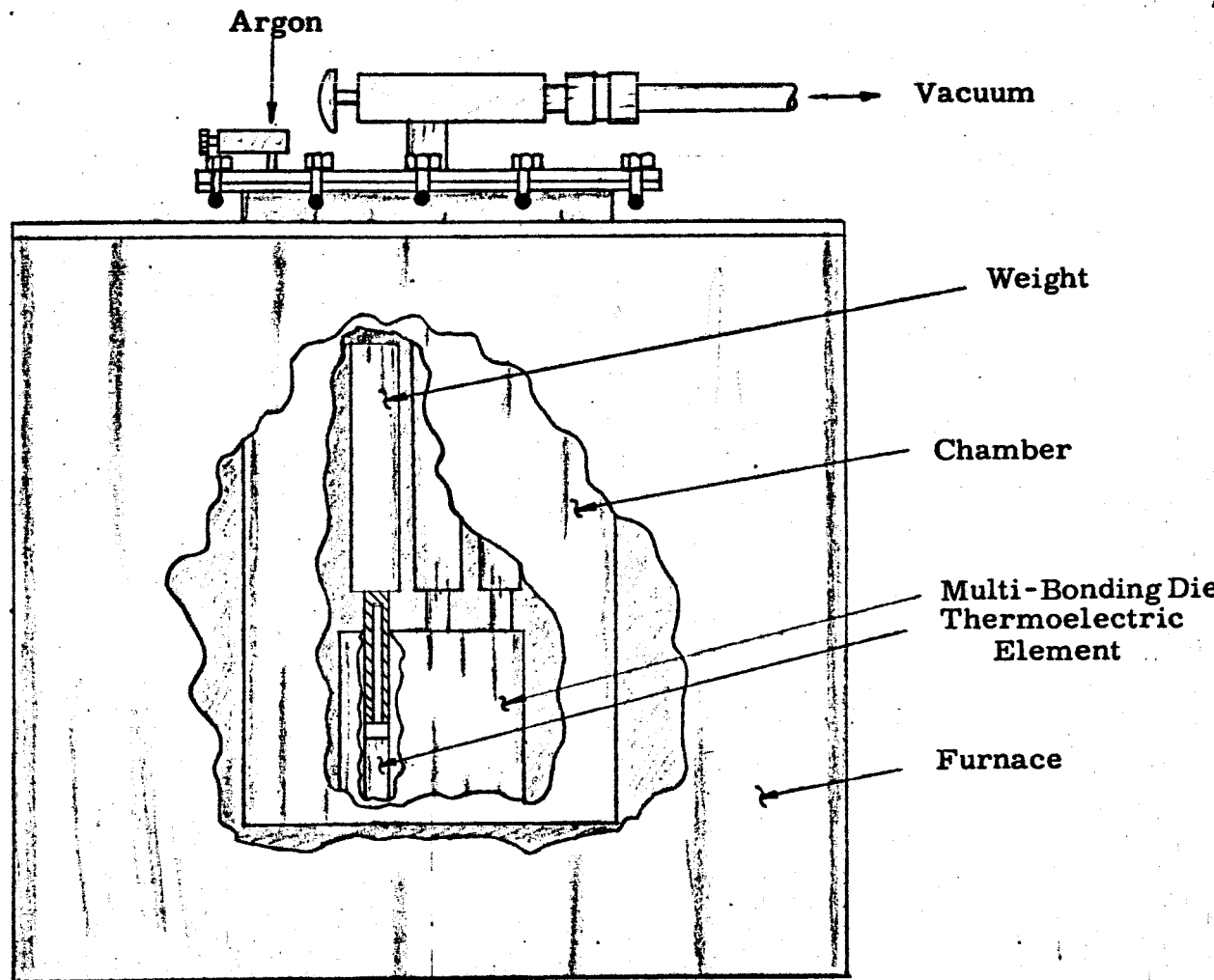


Figure 2. Multiple Element Bonding Fixture

### III. SAMPLE FABRICATION

Toward the end of the last quarter, it was decided to suspend work on TEG-3P p-PbSnTe and to concentrate instead on pure p-PbTe. This decision resulted from the poor results obtained at this laboratory and elsewhere with the PbSnTe material. In general, PbSnTe elements produced at Hittman Associates had low Seebeck Coefficients, were extremely fragile, and fractured during bonding operations.

A lot of TEG-2P p-PbTe powder was received from 3M Company during this quarter. The quality control data supplied with the powder compared with 3M's published values as follows:

	<u>3M Quality Control</u>	<u>3M Published Values</u>	<u>Deviation From Published Values</u>
Room Temp. Resistivity	198 $\mu\Omega$ in.	170 $\mu\Omega$ in.	+ 16.4%
Seebeck Voltage at $\Delta T = 600^\circ\text{F}$ $T_c = 75^\circ\text{F}$	64 mv	56 mv	+ 14.3%

The lot properties were not within + 10 percent of the published data. However, samples were prepared at Hittman Associates and room temperature resistivity and low temperature Seebeck Coefficient were measured. These values, for both parameters, were lower than the published values. Figure 3 shows the measured properties of p-PbTe elements produced at Hittman Associates. The Seebeck Coefficients are shown as percent deviation from the published 3M values. Deviations are consistently less than 10 percent and are usually negative in sign. Resistivities, shown in Figure 3 in  $\mu\Omega$  in., were in every case below the published value of 170  $\mu\Omega$  in. and substantially below the lot resistivity of 198  $\mu\Omega$  in. measured by 3M. The difference is undoubtedly due to the much higher density of our hot pressed elements compared to those made by 3M by cold pressing and sintering. Figure 4 shows the porosity observed in a typical 3M TEGS-2P element and the almost fully dense structure achieved at Hittman Associates by hot pressing the 3M supplied powder.

In addition to these p-PbTe elements, a small number of n-PbTe thermoelectric elements were fabricated, primarily for life testing. Seebeck Coefficients for these elements were 10-15 percent below the published value which is close to earlier production. Almost all had resistivities within 10 percent of the mean value of 164  $\mu\Omega$  in. The mean resistivity value measured during the previous quarter was 169  $\mu\Omega$  in. indicating a consistent process. As with the p-PbTe elements discussed above, resistivity of n-PbTe elements is below the published 3M value of 200  $\mu\Omega$  in. or the 3M quality control report value of 195  $\mu\Omega$  in. measured on elements prepared by them from this lot of powder.

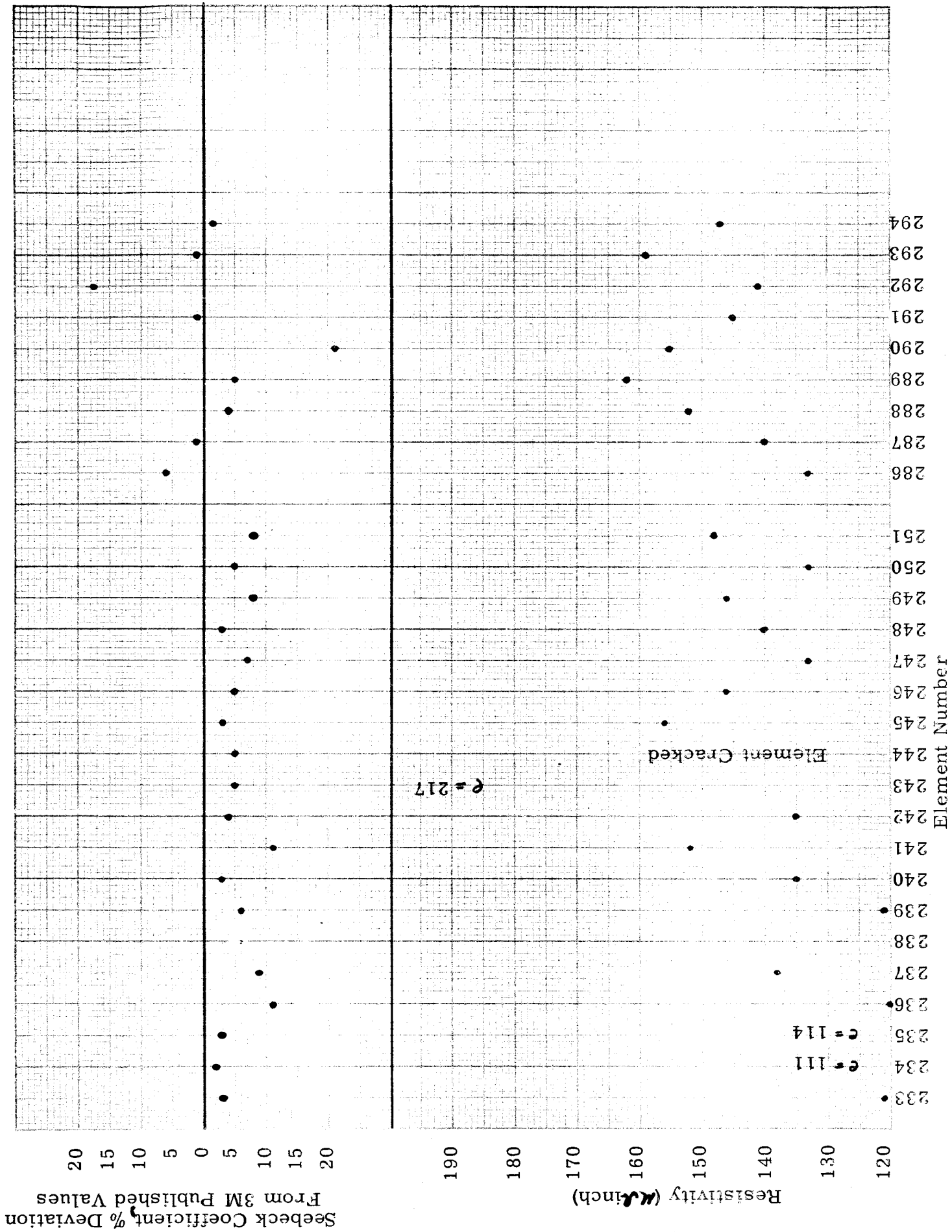
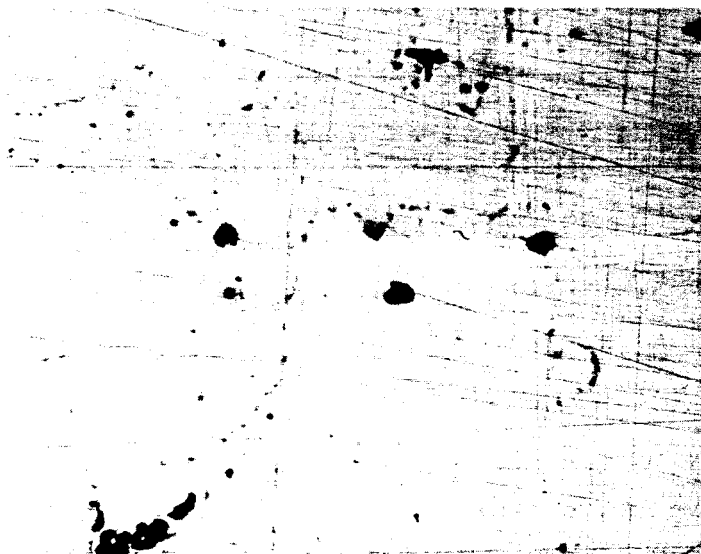
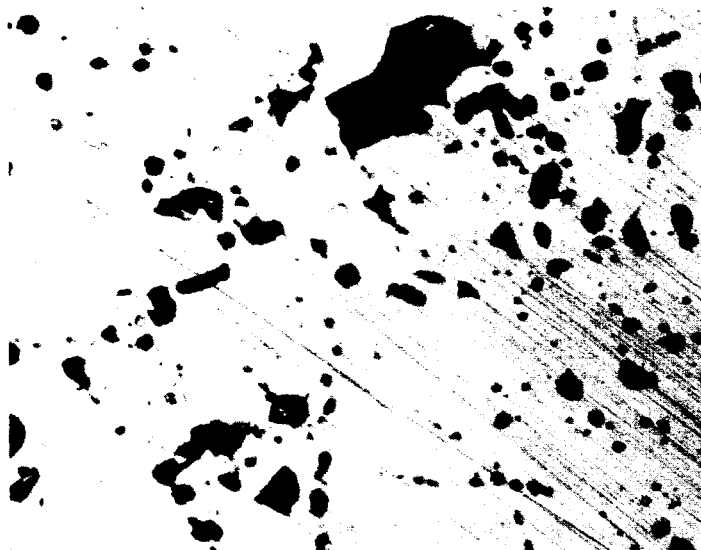


Figure 3. Seebeck Coefficient and Resistivity of TEG-2P Elements  
Produced During September - November 1965



a) TEG-2P Element Hot Pressed at Hittman Associates 130X



b) TEGS-2P Element Cold Pressed and Sintered at 3M 130X

Figure 4. p-PbTe Thermoelectric Elements

#### IV. EFFECT OF ADDITIVES ON p-PbTe

It has been observed at this laboratory and elsewhere that p-PbTe is far more susceptible to failure than n-PbTe and that this situation is due, in part, to the poor strength of the p-type alloy. Although TEG-2P p-PbTe is superior to TEG-3P p-PbSnTe in this respect, it is not comparable to the n-material. For example, almost no n-PbTe fractured during bonding while about one half of the p-type elements broke either during bonding or during handling or measurements subsequent to bonding.

Torsion tests of bonded elements performed earlier in this program and reported in References 1 and 2 showed that n-PbTe is substantially stronger than p-PbTe. Further study of the fractures showed that n-PbTe cracked in the helical pattern typical of failure in torsion indicating that no cracks or stresses approaching the fracture stress were present in the bonded elements. The p-PbTe elements did not display this helical fracture and it was concluded that the stresses generated while cooling from the bonding temperature were sufficient to initiate cracks in the thermoelectric material. Application of the torsion stress merely resulted in propagation of the existing cracks. Thus, the failure did not appear to be that which normally occurs in torsion tests.

From the foregoing, it is apparent that a technique that would increase the strength of p-PbTe, particularly TEG-2P material, without serious effect on its thermoelectric properties would be highly advantageous. It has been observed earlier (Reference 1) that additions of one weight percent of molybdenum or columbium appears to significantly strengthen p-PbTe. It was not known if this behavior was due to the dispersion strengthening effect often observed when fine particles of a second phase are dispersed in a homogeneous matrix or if the observed strengthening resulted from some interaction between the PbTe and the additive.

Since n-PbTe is sub-stoichiometric with respect to tellurium and p-PbTe is formulated with an excess of tellurium, the additive may strengthen p-PbTe by reacting with the excess tellurium and removing some or all of it from the lattice. If the additive reacts strongly with the tellurium, drastic changes in thermoelectric properties can be expected. It is known that molybdenum (Reference 3) and columbium (Reference 4) form several compounds with tellurium. The bond strength of these compounds relative to that of lead telluride is not known. Since no clear analytical explanation could be found for the observed phenomenon, an exploratory program to study the effect of additives on p-PbTe was undertaken. The additives were chosen to represent two groups, metals that might provide a measure of ductility while reinforcing the brittle PbTe and oxides which would presumably act only as dispersion hardeners and would be less likely to strengthen the thermoelectric material.

The materials chosen for study are listed in Table 1 along with the form in which they were incorporated into the p-PbTe powder. Elements were prepared by the usual hot pressing technique with the exception that in each case the additive was blended into the lead telluride powder prior to hot pressing. Additions of 1/2, 1, and 2 weight percent were made with most of the additives. The thermoelectric properties of these samples are shown in Table 2 except

Table 1. Additives to p-PbTe Studied To Date

<u>Additive</u>	<u>Form</u>	<u>Supplier</u>
Molybdenum	-325 mesh powder - 99.9%	Consolidated Astronautics
Molybdenum	0.001" diameter wire chopped to approx. 1/8" lengths	Sylvania Electric
Tungsten	-325 mesh powder - 99.9%	Consolidated Astronautics
Columbium	-325 mesh powder	A. D. Mackay
Al <sub>2</sub> O <sub>3</sub>	-600 mesh powder	City Chemical Company
Al <sub>2</sub> O <sub>3</sub>	Levigated alumina	Buehler, Ltd.
Al <sub>2</sub> O <sub>3</sub>	Sapphire fibers	Thermal Kinetic Fibers
ZrO <sub>2</sub>	Monoclinic fibers	Owens Corning Fiberglass
ThO <sub>2</sub>	Produced by calcining reagent grade Th(NO <sub>3</sub> ) <sub>4</sub> · 4H <sub>2</sub> O	J. T. Baker



Table 2. Thermoelectric Properties of p-PbTe Containing Additives

Additive	Seebeck Coefficient Data			Room Temperature Electrical Resistivity $\mu\Omega$ in.	Comments
	Temp. °C	S, $\mu$ V/°C	% Deviation from p-PbTe		
1% Cb	90 152	92 135	-9.8 -6.3	140	
2% Cb	96 157	110 146	+3.6 -0.7	300	Sample apparently cracked or inhomogeneous
2% Cb	103 165	95 131	-10.4 -16.0	445	
1/2% W	94 140	101 138	-3.8 +1.5	174	
1% W	103 139	106 133	-4.5 +1.5	172	
2% W	102 158	109 157	-0.9 +6.1	180	
1/2% Al <sub>2</sub> O <sub>3</sub> fibers	100 145	102 138	-7.3 -0.7	339	Sample apparently cracked
1% Al <sub>2</sub> O <sub>3</sub> fibers	97 164	104 156	-2.8 +2.6	134	
1% Al <sub>2</sub> O <sub>3</sub> powder	98 153	99 144	-8.3 0	100	
2% Al <sub>2</sub> O <sub>3</sub> powder	101 157	100 143	-8.2 -2.7	144	
1% ZrO <sub>2</sub> fibers	106 157	105 152	-7.1 +3.4	135	
1/2% ThO <sub>2</sub>	89 141	101 135	0 -0.7	154	
1% ThO <sub>2</sub>	90 143	91 131	-10.8 -5.1	103	Appeared inhomogeneous
2% ThO <sub>2</sub>	78 135	105 143	+11.7 +20.1	131	11.

for those of the elements containing molybdenum which are shown in Figure 5. From Table 2 it is clear that most of the additives had little effect on the as-pressed thermoelectric properties of p-PbTe. Addition of 2 percent columbium resulted in unacceptably high resistivity. The sample containing 1/2 percent  $\text{Al}_2\text{O}_3$  fibers also had high resistivity but other  $\text{Al}_2\text{O}_3$  containing thermoelectric elements were satisfactory, so this result was discounted. The sample containing 2 percent  $\text{ThO}_2$  had unusually high Seebeck Coefficient indicating possible poisoning. The properties of the samples containing molybdenum did not differ appreciably from p-PbTe without additives. Resistivity of elements containing 0.001" wire was somewhat higher than those to which the molybdenum was added as powder.

Several of the samples containing additives were subjected to a 100 hour isothermal test at approximately 920°F. Each element was sealed in an individual vycor capsule under argon atmosphere. The thermoelectric properties before and after this test are shown in Table 3. There were some changes in the properties of all the elements including the control sample containing no additive. None of the changes were so consistent or severe that any additive could be clearly disqualified from further consideration on the basis of this test.

A number of elements containing additives were bonded to iron shoes and tested in torsion at room temperature. These test results are shown in Table 4. It is clear that molybdenum fibers are particularly effective in strengthening p-PbTe and that molybdenum powder and  $\text{Al}_2\text{O}_3$  fibers also strengthen p-PbTe. Further tests will be necessary to determine whether tungsten additives are beneficial. Metallography of these samples is not yet complete and results will be reported during the next period.

Tentative conclusions to be drawn from the results obtained to date are that p-PbTe can be appreciably strengthened by the use of additives without objectionably large changes in initial thermoelectric properties. Life tests of samples containing molybdenum fibers are underway and so more definitive results can be expected during the next quarter.

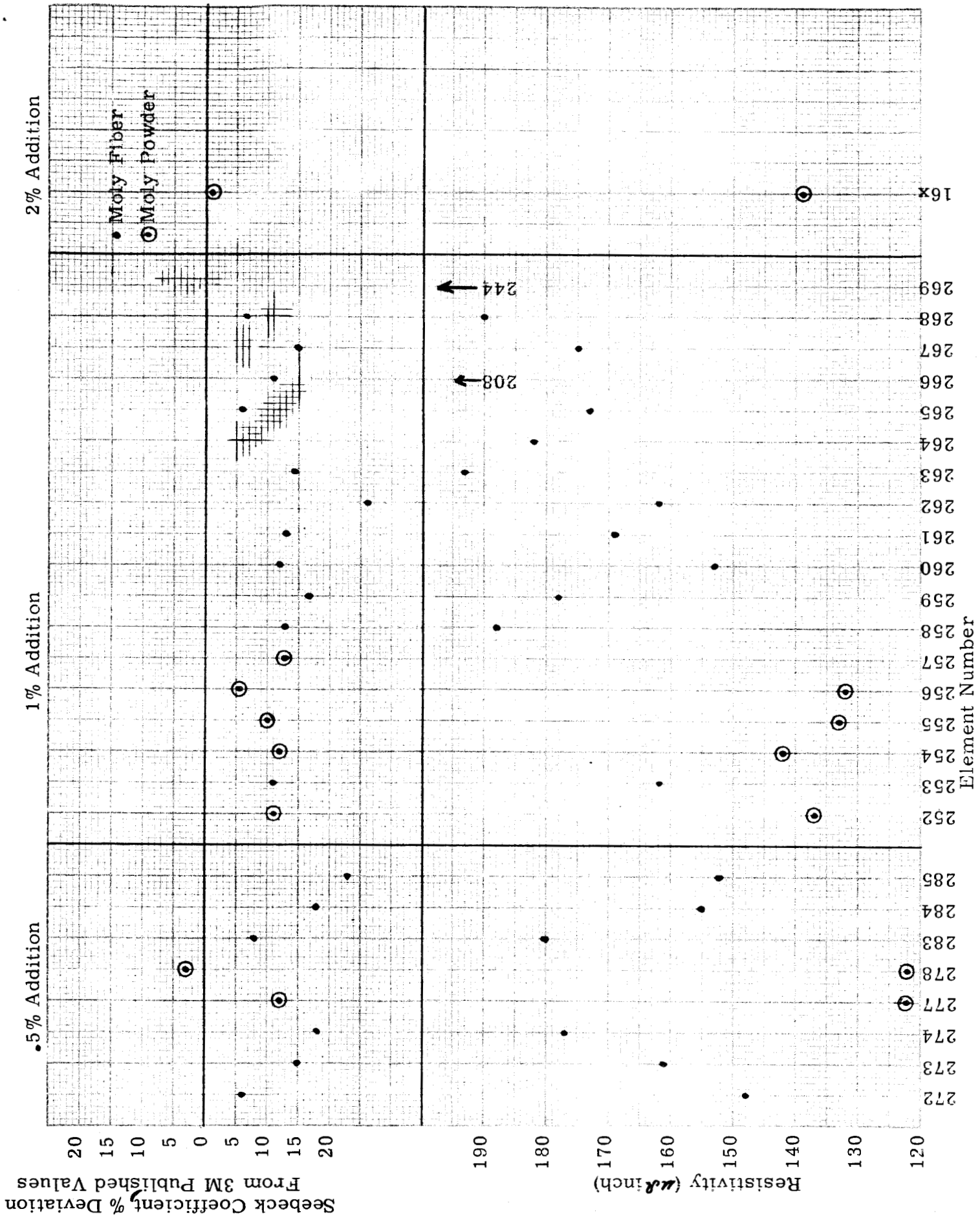


Figure 5. Seebeck Coefficient and Resistivity of p-PbTe Thermoelectric Elements Containing Molybdenum Additions

Table 3. Effect of 100 Hours at 920°F On The

Additive	Seebeck Coefficient Data As Pressed			T
	Temperature	S, $\mu\text{V}/^\circ\text{C}$	% Deviation from 3M Data	
1% Mo fibers	92	89	-14.4	
	137	123	-8.2	
1% Mo powder	100	95	-12.8	
	160	140	-2.8	
2% Mo powder	96	110	+3.8	
	154	138	-4.8	
1% W	103	106	-4.5	
	139	133	-1.5	
2% W	102	109	-0.9	
	158	157	+6.1	
1% Al <sub>2</sub> O <sub>3</sub> fibers	97	104	-2.8	
	164	156	+2.6	
1% Al <sub>2</sub> O <sub>3</sub> powder	98	99	-8.3	
	153	144	0	
2% Al <sub>2</sub> O <sub>3</sub> powder	101	100	-8.2	
	157	143	-2.7	
1% ZrO <sub>2</sub> fibers	106	105	-7.1	
	157	152	+3.4	
1% ThO <sub>2</sub>	90	91	-10.8	
	143	131	-5.1	
2% ThO <sub>2</sub>	78	105	+11.7	
	135	143	+20.1	
p-PbTe	96	101	-4.7	
No additive	148	139	-1.4	

(2)

14.

## Thermoelectric Properties p-PbTe Containing Additives

Temperature	Seebeck Coefficient Data After 100 Hour Test		Room Temp. Resistivity $\mu\Omega$ in.	
	S, $\mu V/^{\circ}C$	% Deviation from 3M Data	As Pressed	After 100 Hr. Test
99	90	-16.7	162	146
157	130	-11.6		
89	96	-4.9	137	161
146	142	+1.4		
100	93	-14.7	139	106
161	134	-10.7		
99	137	+26.8	172	170
152	185	+28.5		
92	106	+1.9	180	157
150	155	+9.2		
87	114	+14.0	134	182
145	159	+14.4		
97	119	+11.2	100	181
149	171	+20.2		
92	104	0	144	188
152	154	+7.6		
97	114	+5.5	135	196
151	157	+9.8		
94	113	+7.6	103	264
150	159	+12.0		
95	117	+10.4	131	171
148	158	+12.1		
101	125	+13.6	134	171
147	152	+8.6		

Table 4. Effects of Additives On The Torsion Strength of p-PbTe

<u>Additive</u>	<u>Torsion Strength, psi</u>	<u>Remarks</u>
1/2% Mo fibers	850	Helical fracture
1/2% Mo fibers	700	Sample corroded during bonding
1% Mo fibers	1080	Helical fracture
1/2% Mo powder	300	Sample corroded during bonding, crack present prior to test
1/2% Mo powder	400	Sample broke into several pieces
2% Mo powder	850	Broke in element adjacent to bond
1/2% W	550	Crack initiated at corrosion Typical p-PbTe fracture
1/2% Al <sub>2</sub> O <sub>3</sub> fibers	850	Helical fracture; many chips fell out
1% Al <sub>2</sub> O <sub>3</sub> fibers	400	Broke in braze
1% Al <sub>2</sub> O <sub>3</sub> powder	300	Broke in element near interface
2% Al <sub>2</sub> O <sub>3</sub> powder	300	Broke in braze
1% ZrO <sub>2</sub> fibers	300	Broke in element
1% ThO <sub>2</sub>	250	Broke in element near interface
2% ThO <sub>2</sub>	400	Separated at interface; element cracked
p-PbTe no additive	400	Both samples failed in a manner typical of previous p-PbTe elements tested
p-PbTe no additive	400	

## V. LIFE TESTS OF THERMOELECTRIC ELEMENTS

During this quarter, post test evaluation was completed on the 200 hour and 500 hour life tests of n-PbTe elements reported previously (Reference 2). Four additional life tests were started during the period, two of n-PbTe elements scheduled for 1000 and 5000 hours and two of p-PbTe elements scheduled for 500 and 1000 hours. Of these, only the 500 hour test of p-PbTe was completed. The others continue on test.

### A. Post Test Evaluation of n-PbTe

The 200 hour and 500 hour tests of n-PbTe showed that no degradation occurs during this period of time. Metallographic examination showed that although no diffusion was observed, cracks were present at or near the bond interfaces in several elements. These samples were mounted for examination by the conventional heat and pressure technique and it is believed that the mounting operation was responsible for the cracking. Subsequent elements prepared by the cold mounting process in which no pressure is applied did not appear to be cracked. Two metallographic mounts, one from the 200 hour test and the other from the 500 hour test, were studied by the electron microprobe technique by L. Kobren of Goddard Space Flight Center.

Figures 6 and 7 are pictorial representations of the results of this study on the 500 hour test sample. The light and dark areas are an electron back-scatter picture of the bond zone in the thermoelectric element. Areas containing high atomic weight atoms, as those in PbTe, appear white in the picture and low atomic weight areas, such as iron, are black. The braze zone is seen to be of intermediate weight. The grid spacing on these photographs is 40 microns (approximately 1.6 mils). The sample was bombarded with electrons along the horizontal path shown as a white line toward the center of each picture. This bombardment results in the generation of x-rays characteristic of the individual elements contained in the area being bombarded, the intensity of each x-ray being proportional to the concentration of the element from which it is generated. Thus, Figure 6 shows the distribution of iron, lead and tin in the bond area after 500 hours of operation and Figure 7 repeats the iron traverse and shows tellurium and titanium distributions under the same conditions. The various transverse are displaced vertically for clarity of presentation. The observations made from these data were:

1. There is no diffusion of any component of the braze or thermoelement into the iron shoe.
2. Iron is present in the braze zone for a distance of at least 20 microns (approximately 0.8 mils) and is distributed inhomogeneously. No iron is found in the PbTe.
3. Titanium is found only in the braze zone (to which it is added as one weight percent) and is present as discrete particles. There appears to be some association of iron with titanium based on the coincidence of the peaks for both these elements.

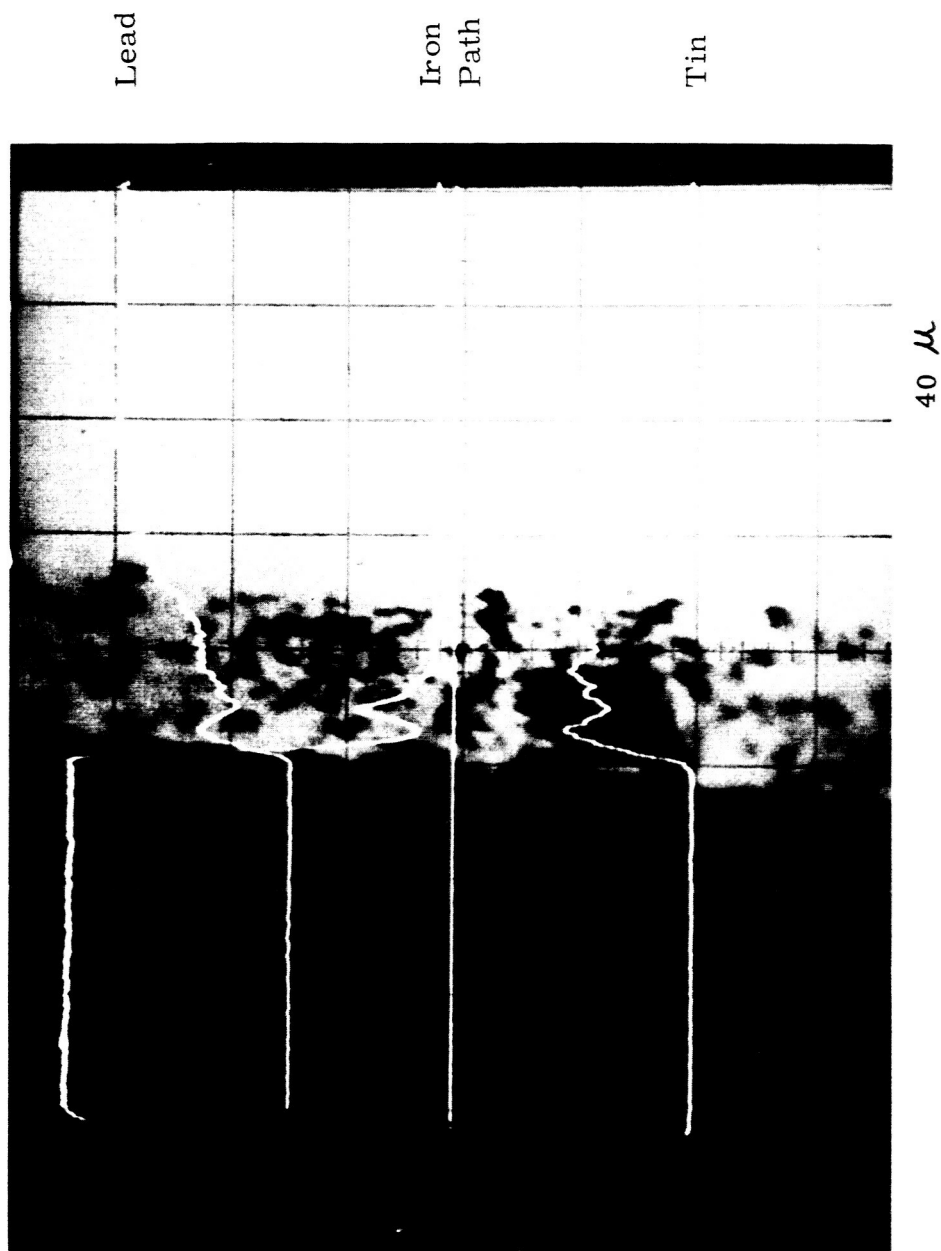
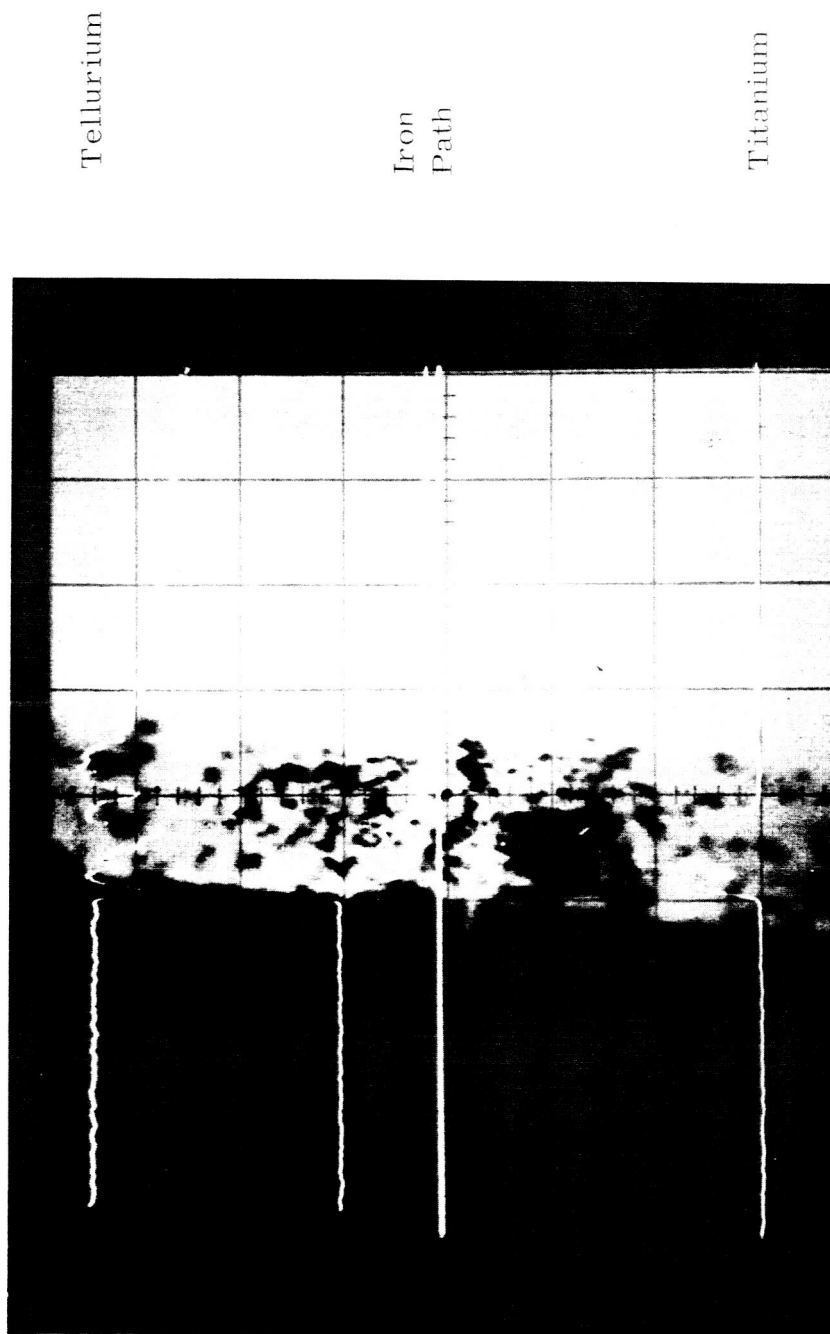


Figure 6. Electron Microprobe Traverse of Hot Junction of n-PbTe Thermoelectric Element After 500 Hour Life Test  
Showing Concentration of Iron, Lead and Tin





Tellurium

Iron  
Path

Titanium

Figure 7. Electron Microprobe Traverse of Hot Junction of n-PbTe  
Thermoelectric Element After 500 Hour Life Test  
Showing Concentration of Iron, Titanium and Tellurium

4. Tellurium content is uniform across the braze (the presence of titanium particles results in an indication of tellurium depletion). There is an increased tellurium concentration in the PbTe adjacent to the braze zone. This may result from diffusion of lead from the thermoelement into the braze.
5. Lead was present completely across the braze, the concentration steadily increasing in areas closest to the PbTe.
6. Tin had diffused approximately 100 microns (approximately 4 mils) into the lead telluride.

Similar results were obtained when measurements were made at the hot junction of the 200 hour test sample. The extent of the diffusion was less in this shorter time run. For example, tin was found to have penetrated only 32 microns (approximately 1.3 mils) into the PbTe compared to 100 microns in the 500 hour sample.

An electron microprobe study was also made of the cold shoe of the 200 hour life test sample. This iron shoe had been brazed to the lead telluride with pure tin. The bond area is represented pictorially in Figure 8 which was made in the same manner as Figures 6 and 7 described above. No iron or lead diffusion can be observed and that of tin is minimal. A substantial tellurium concentration (approximately 23% of the tellurium value in PbTe) was found uniformly distributed in the braze. This may be an anomaly caused during sample preparation, but more likely occurred during the bonding process.

#### B. p-PbTe Life Tests

The first life test of p-PbTe thermoelements was performed during this period. Four elements, two bonded and two unbonded, were tested at hot junction temperatures of 970-1000°F and cold side temperatures of approximately 110°F for 500 hours. These elements were similar in appearance to those described in Reference 2 except that the cold side bond was identical to the hot junction bond. Both were made simultaneously in a single operation avoiding the tin soldering step used previously.

The bonded elements were a 3M produced TEGS-2P p-PbTe sample and a Hittman Associates sample, hot pressed from TEG-2P powder but containing, in addition, one weight percent molybdenum fibers. The unbonded elements were produced at Hittman Associates, one being p-PbTe with no additive and the second containing one percent molybdenum fibers.

Figures 9 through 12 show the performance of these elements during the life test. It can be seen that open circuit voltage either increased slightly or remained constant during the 500 hour test. Power output of the two bonded samples (the only ones for which power was measured) dropped about 7 to 10 percent. Table 5 compares the properties of the test elements in the as-pressed, as-bonded, and post-life conditions. Unlike the n-PbTe samples tested previously, in which measured property changes were within the error limits of the test equipment, substantial property changes were observed in the p-PbTe test samples. Resistivity of the bonded molybdenum containing

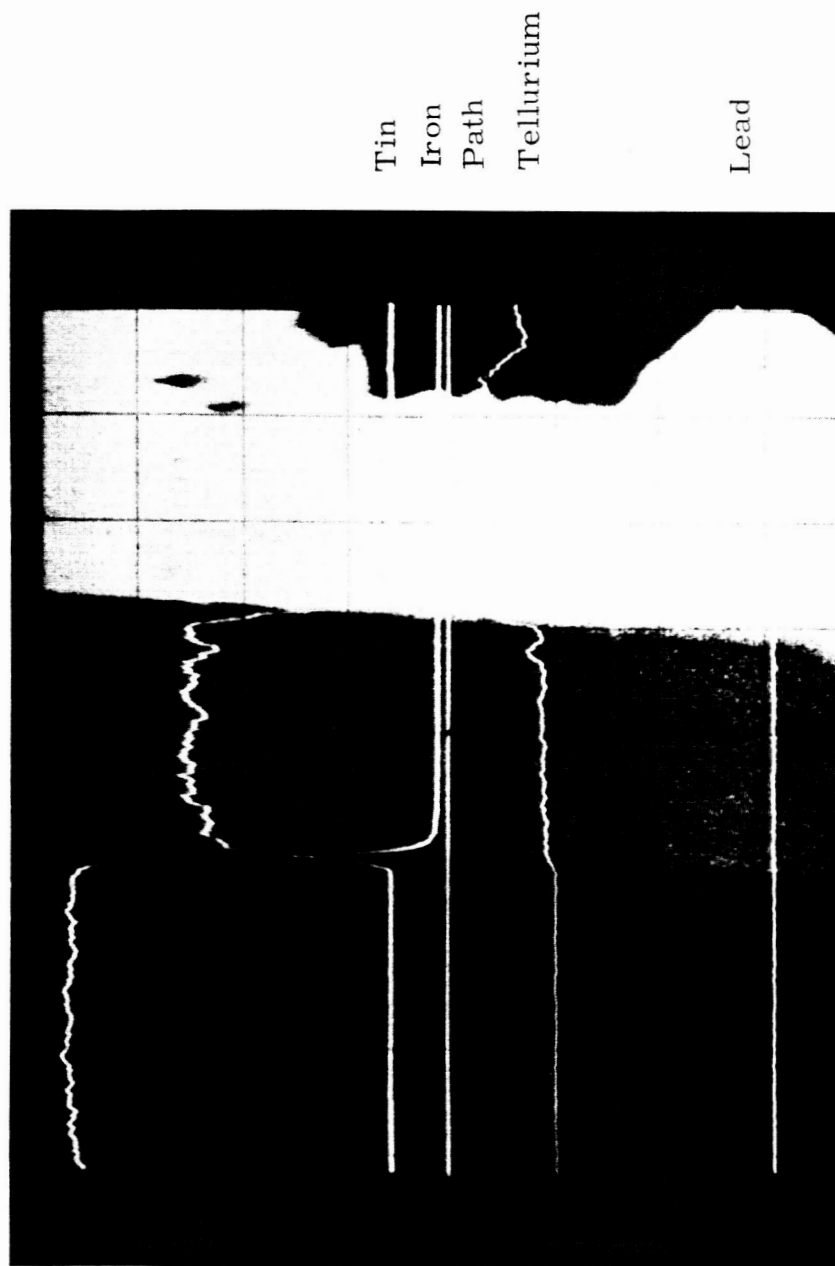


Figure 8. Electron Microprobe Traverse of Cold Junction of n-PbTe Thermoelectric Element After 200 Hour Life Test

Sample 253A, PbTe-2P + 1% Mo Fibers; Unit #1; Position 3

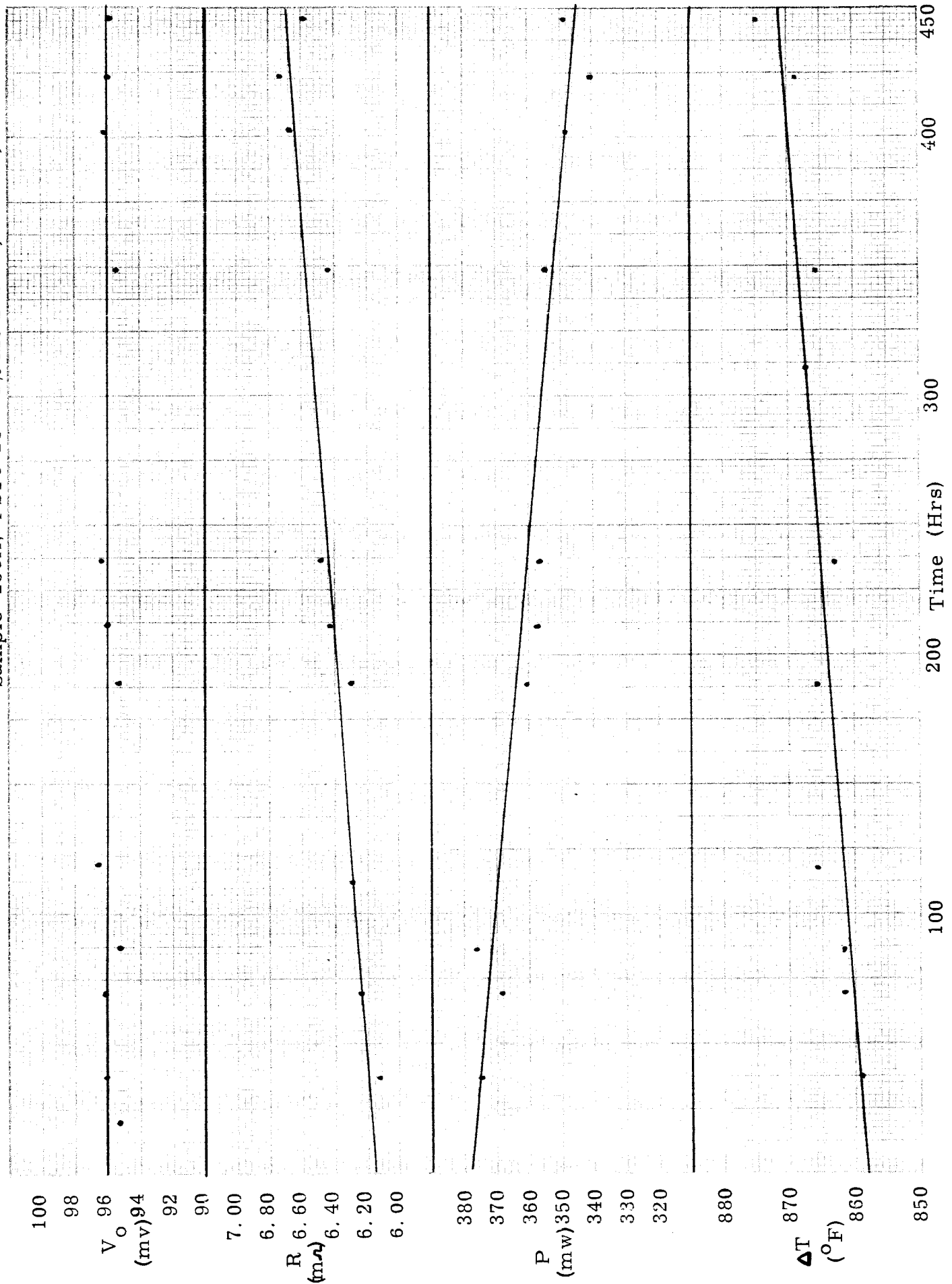


Figure 9. Performance of p-PbTe Element No. 253A During 500 Hour Life Test

Sample 3M #2-2P; Unit #1; Position 4

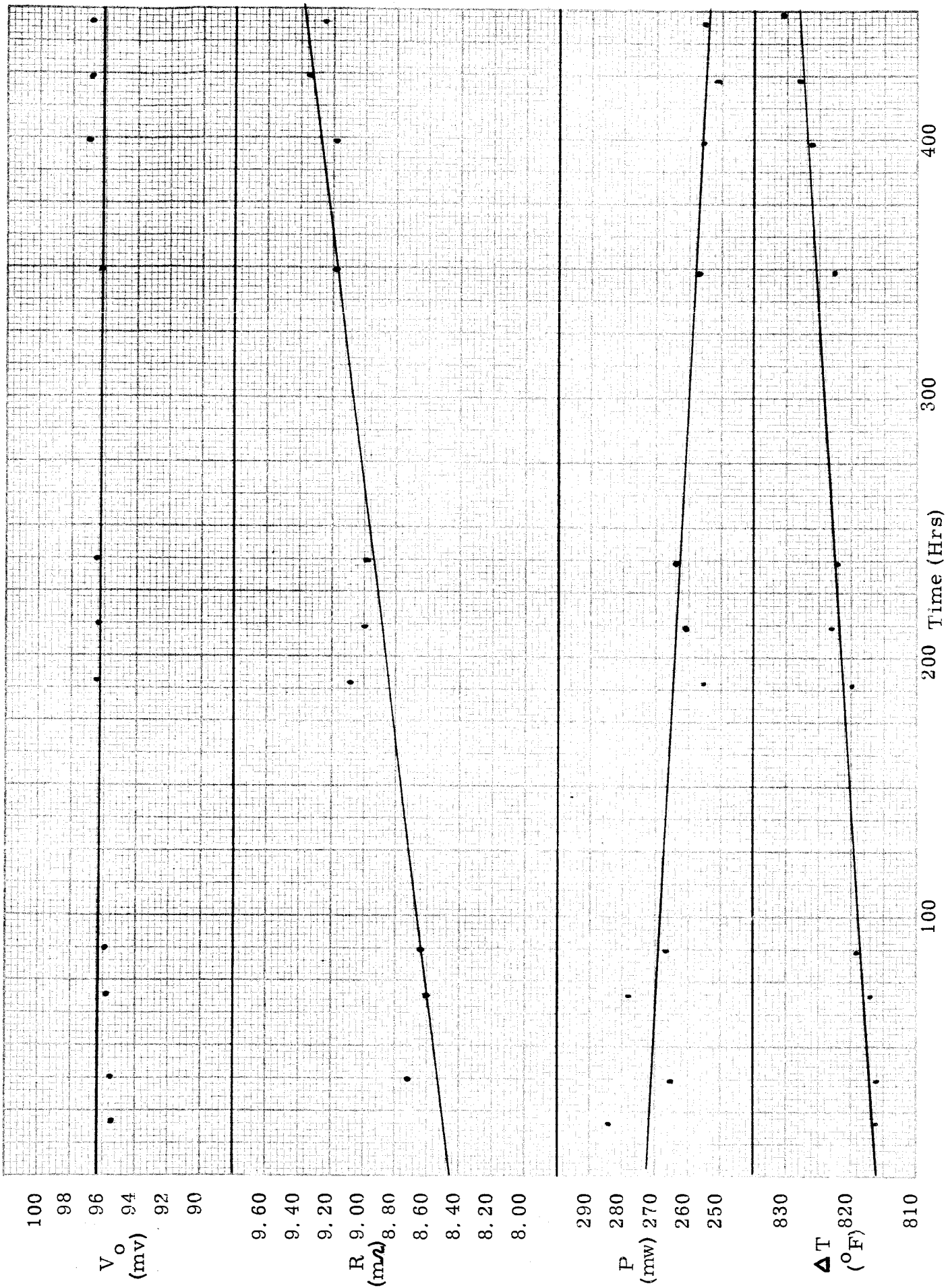


Figure 10. Performance of p-PbTe Element No 3M - #2 During 500 Hour Life Test

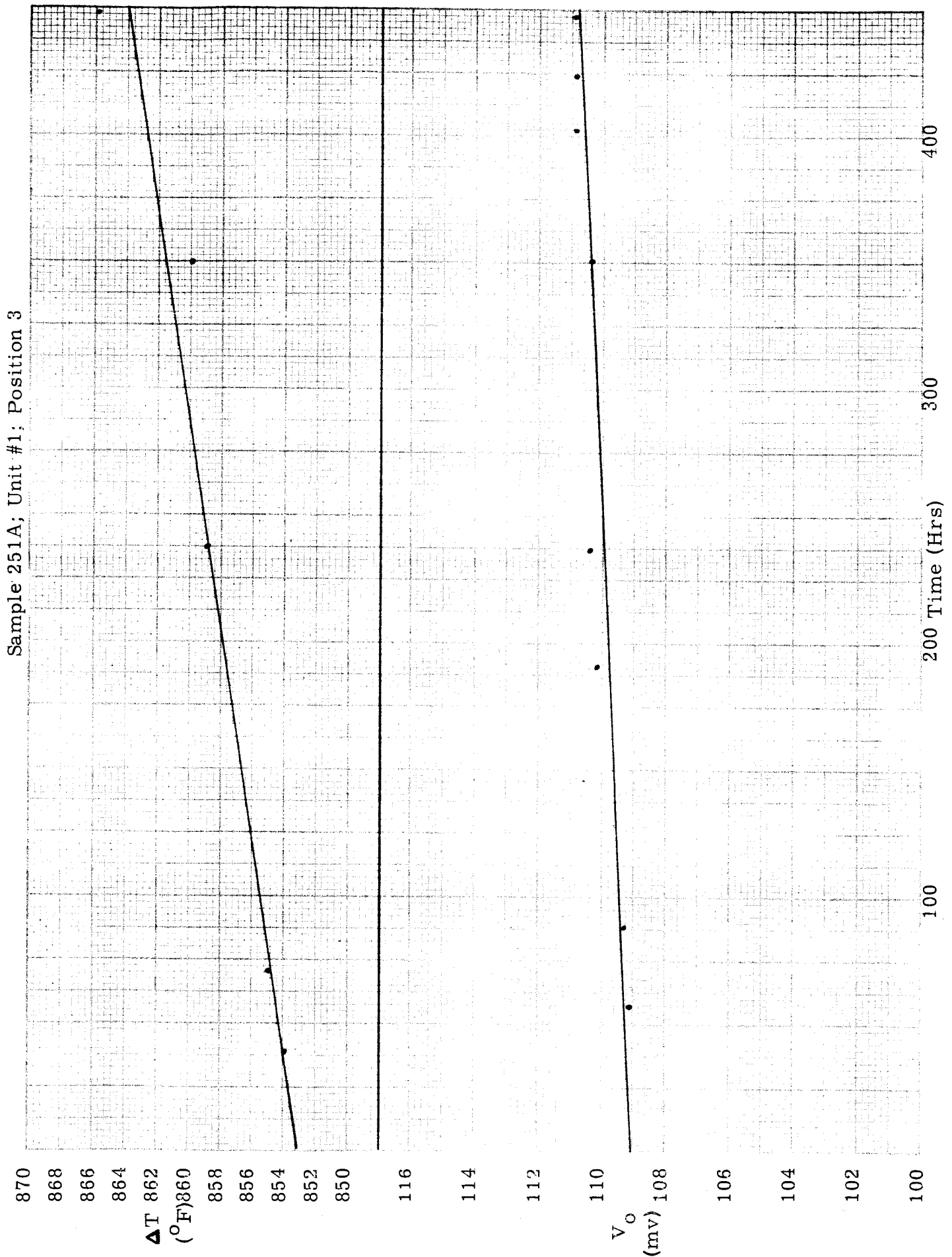


Figure 11. Performance of Unloaded p-PbTe Element No. 251A

Sample 267A; Unit #1; Position 5

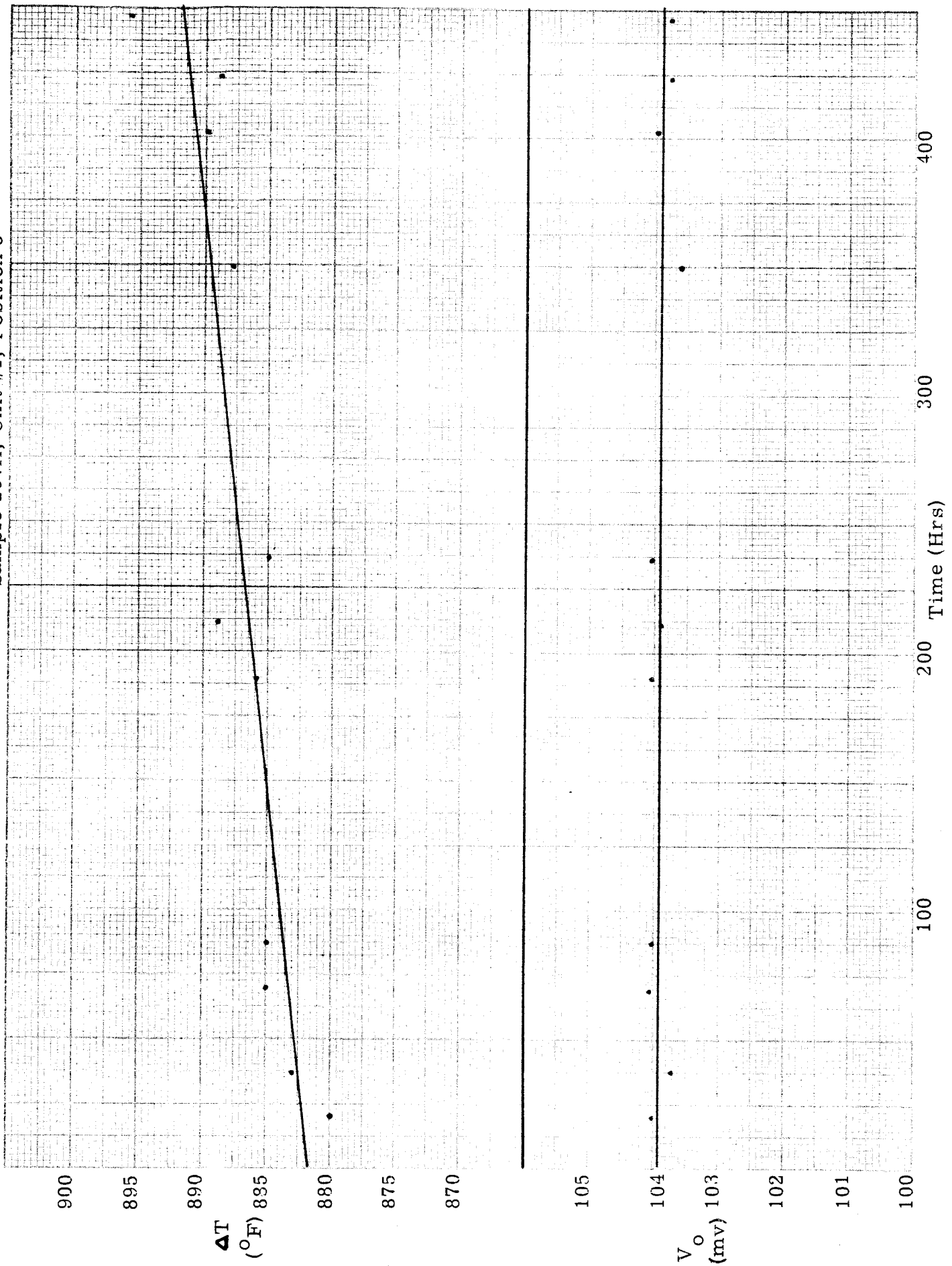


Figure 12. Performance of Unbonded p-PbTe Element No. 267A During 500 Hour Life Test

25 ①

Table 5. Properties of p-PbTe

Sample No.	Composition	Bond Resistance $\mu\Omega$				Room Temp. Resistivity $\mu\Omega$ in.			As Pressed		
		Before Test		After Test		As Pressed	As Bonded	After Life Test	Temp °C	S, $\mu V/^\circ C$	%Dev
		Hot	Cold	Hot	Cold						
251A	p-PbTe	-	-	-	-	148	-	116	94 153	95 140	
253A	p-PbTe + 1 w/o Mo fibers	105	115	210	1140	162	249	220	92 137	89 123	
3M-2P- #2	TEGS-2P, p-PbTe	190	180	0	Sepa- rated	163	162	192	96 150	82 123	
267A	p-PbTe + 1 w/o Mo fibers	-	-	-	-	175	-	148	93 160	85 131	



2

bTe Thermoelements Tested For 500 Hours

Seebeck Coefficient Data

d	As Bonded			After Life Test		
	from 3M Values	Temp <sup>o</sup> C	S, $\mu$ V/ <sup>o</sup> C %Dev. from 3M Values	Temp <sup>o</sup> C	S, $\mu$ V/ <sup>o</sup> C %Dev. 3M Values	
	-13.7	-	-	98	118	+9.3
	-3.5	-	-	153	157	+9.0
	-14.4	80	97	72	113	+25.6
	-8.2	124	127	124	128	+2.4
	-19.8	69	87	73	81	-11.0
	-13.4	121	122	120	113	-7.4
	-18.2	-	-	103	96	-13.5
	-12.1	-	-	171	121	-22.4

element increased by 50 percent during bonding but both samples containing the additive had lower resistivity after the life test than before. The p-PbTe element, without additives, also had substantially lower resistivity after the test. The bonded 3M element, however, showed a 19 percent increase in resistivity. Seebeck test results also indicated changes. The Seebeck Coefficient of the unbonded element, without additives, showed a substantial increase while the element containing molybdenum decreased somewhat. The bonded element containing molybdenum increased its Seebeck Coefficient during bonding and may have increased it further during the life test, at least at lower temperatures. The Seebeck Coefficient of the 3M element also increased during bonding, but decreased almost to the as-pressed values during life testing.

Metallographic examination of these samples following the life test disclosed the presence of a reaction zone around each molybdenum particle. The appearance of the bonded sample is shown in Figures 13a and 13b and the unbonded sample in Figure 14. The reaction appeared to be uniform through each sample and to be of greater extent in the bonded sample. If the reaction occurred during the life test, the reaction zone would be greater in those areas where the temperature was highest. Since this was not observed, it was concluded that the reaction is largely confined to the hot pressing and bonding operations when the element sees temperatures of approximately 1500°F. This is confirmed by the observation of greater reactions in the bonded element. Both samples will be sent to Goddard Space Flight Center for electron probe analysis.

The hot shoe bond zones appeared to be completely intact in both bonded samples. There was no evidence of cracking or extensive diffusion.

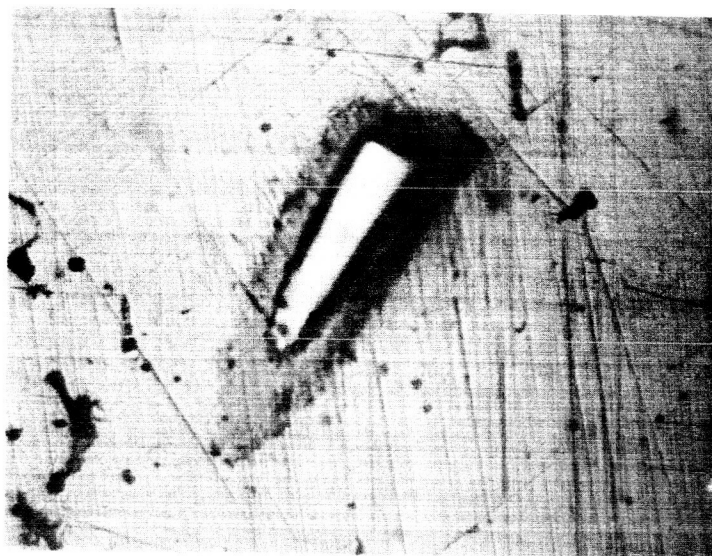
A second life test of p-PbTe elements was started late in the quarter. This run is scheduled for 1000 hours and will be discussed in the next report in this series.

### C. n-PbTe Life Tests

Two life tests of n-PbTe elements are now in progress. The first has completed more than 2000 hours of a scheduled 5000 hour run and the second was started toward the end of the quarter on a 1000 hour test.

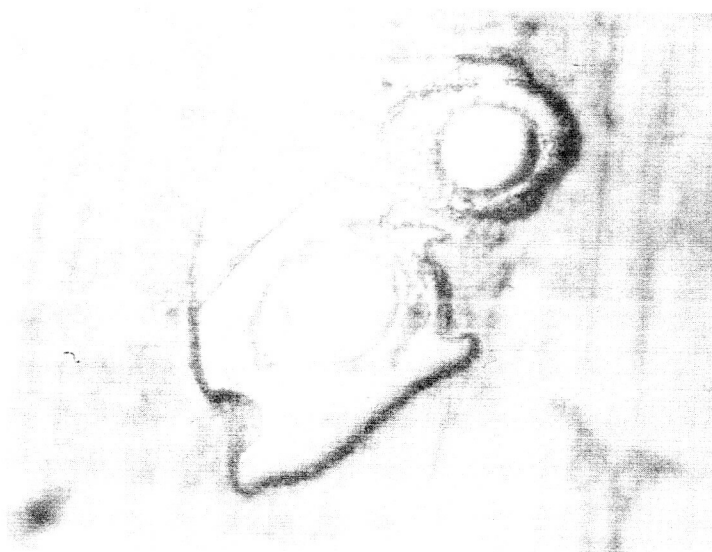
The elements on test in the 5000 hour experiment include three Hittman Associates produced TEG-2N elements bonded to iron shoes, one 3M produced TEGS-2N element bonded at the hot end only, and two unbonded controls, one produced by Hittman Associates, and the other purchased from 3M Company. Before the test was begun, several attempts were made to solder a cold shoe to the bonded 3M element. Considerable difficulty was encountered and rather than delay the test, it was decided to proceed with the samples as described above. The problem of attaching cold end contacts has now been circumvented by bonding both shoes in a single step. This process was described earlier in the report.

Figures 15 through 17 show the performance to date of the bonded test elements. From this figure, it is obvious that total resistance (element plus bond resistance) has been dropping steadily while voltage output has remained practically constant. A break in a water line elsewhere in our building caused



a) Near Hot Interface

520X



b) Near Cold Interface

520X

Figure 13. Bonded p-PbTe + 1% Mo Showing Reaction Zones  
After 500 Hour Life Test

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Figure 14. Unbonded p-PbTe + 1% Mo Element Showing Reaction Zone  
After 500 Hour Life Test (520X)

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Sample 197A; Unit #2; Position 2

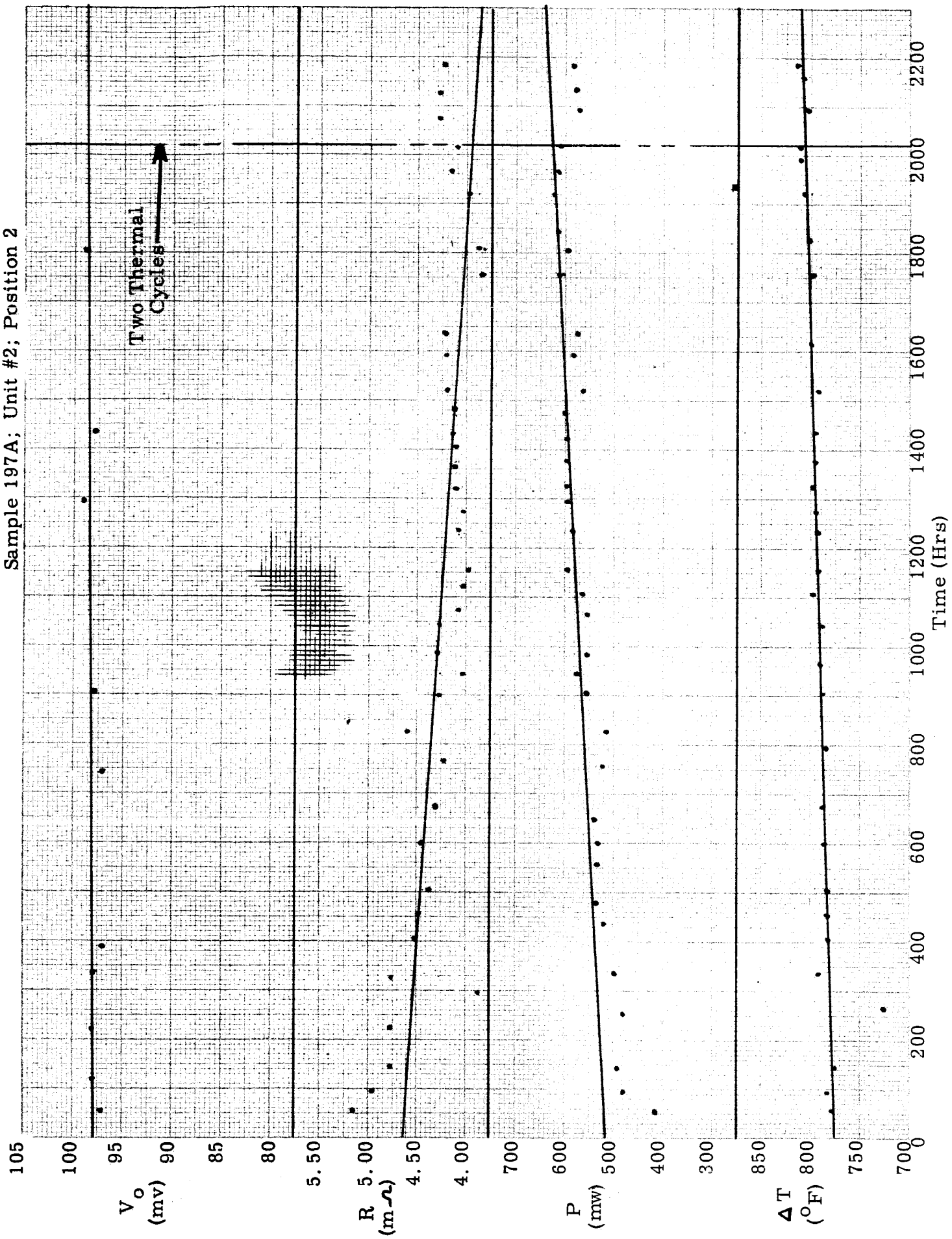


Figure 15. Performance to Date of n-PbTe Element No. 197A During Life Test

Sample 186A; Unit #2; Position 4

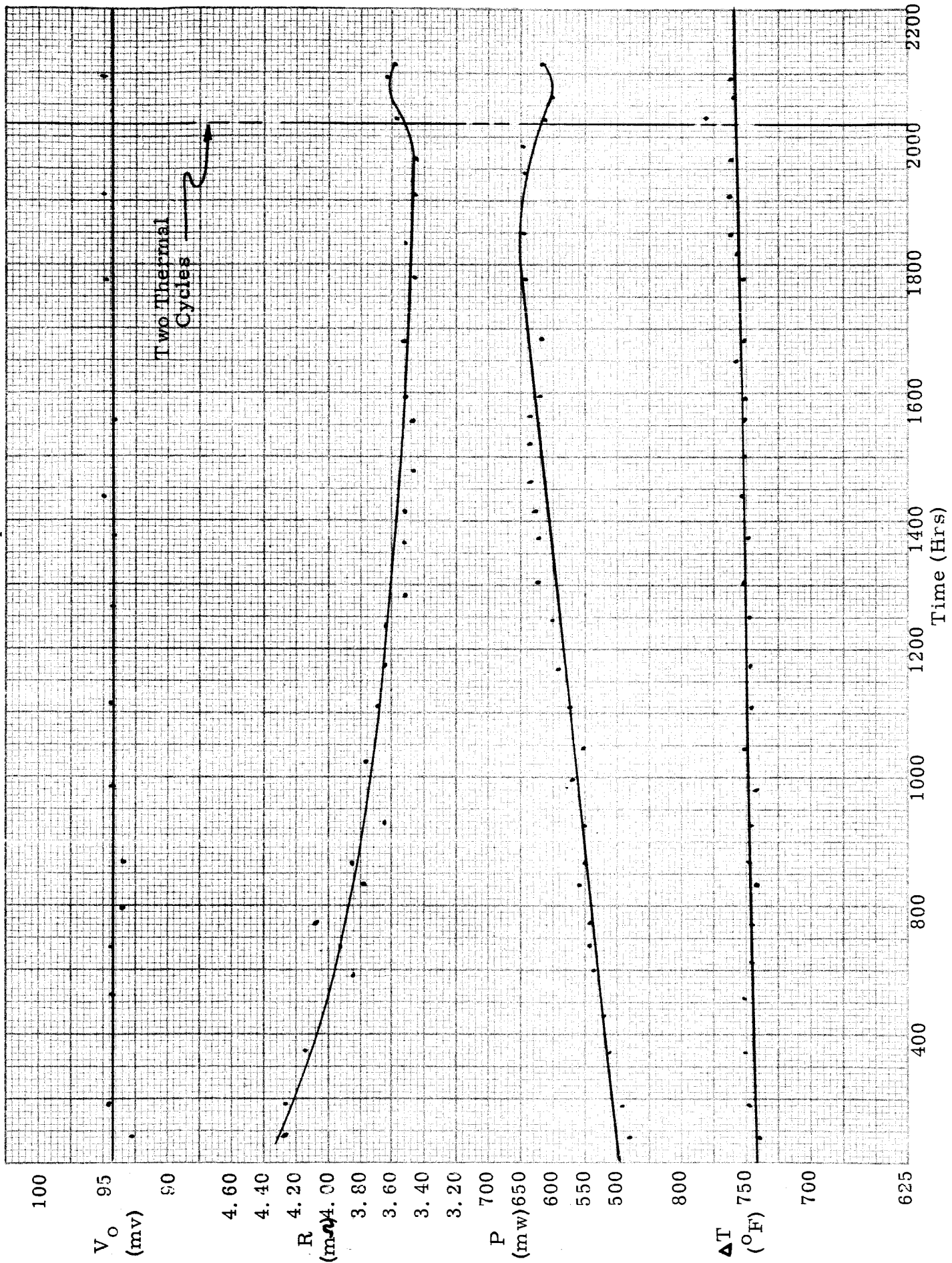


Figure 16. Performance to Date of n-PbTe Element No. 186A During Life Test

Sample 189A; Unit #2; Position 6

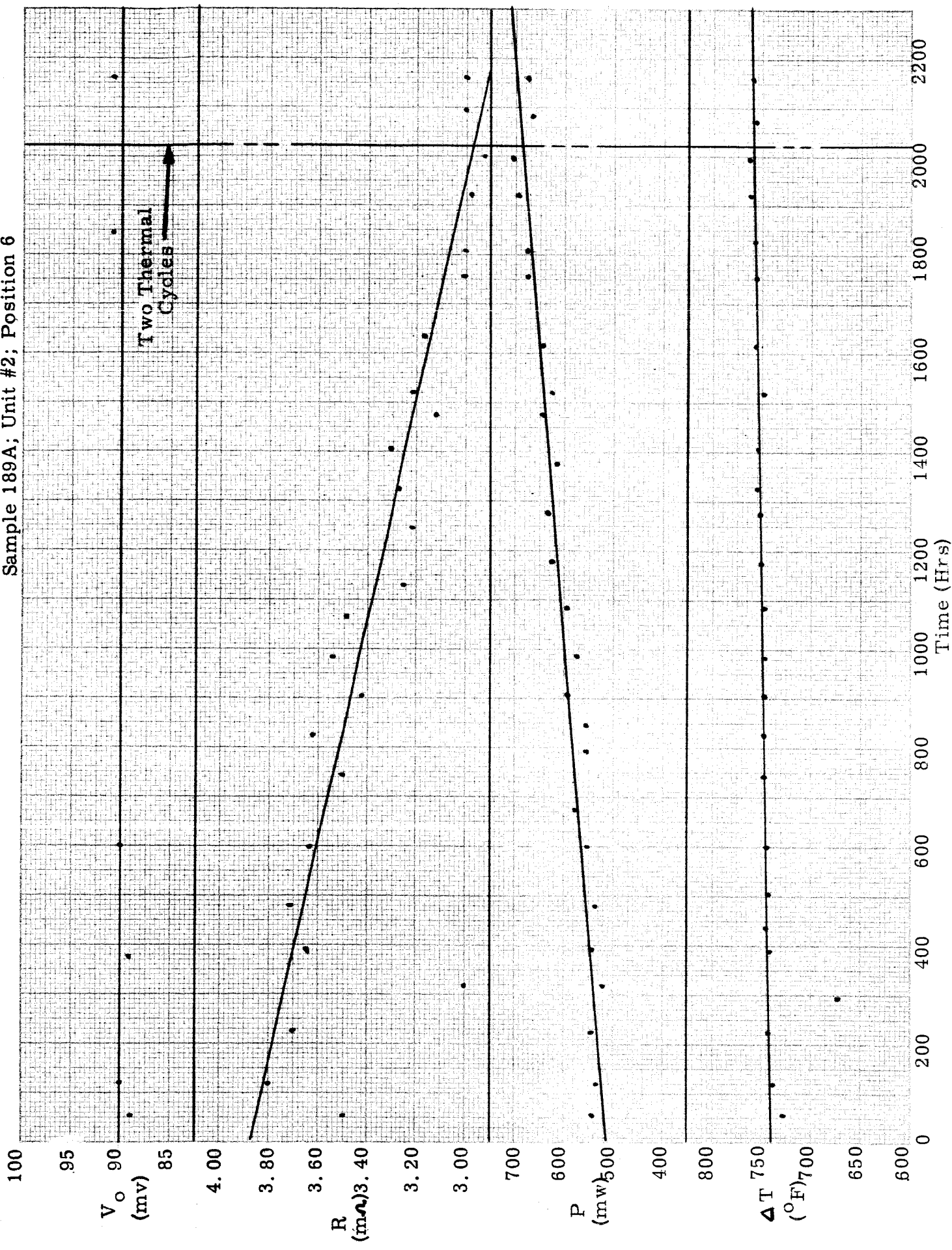


Figure 17. Performance to Date of n-PbTe Element No. 189A During Life Test

temporary loss of water to the tester at the end of the quarter. This, in turn, caused the power to the unit to be shut down and two thermal cycles resulted. Subsequent readings showed slightly higher resistances but further data are required to see if the pre-cycle values will be recovered.

Results of the 1000 hour life test of n-PbTe will be reported during the next period.



## VI. DISCUSSION OF RESULTS

The results obtained during this quarter confirm our earlier conclusions that n-PbTe can be satisfactorily bonded to iron shoes with titanium modified SnTe braze. A detailed description of the process is included in this report. Torsion test results show that bonds formed in this manner are stronger than the thermoelectric elements and that the stresses resulting from the bonding operation do not approach the fracture strength of the PbTe material.

Life tests of bonded n-PbTe elements have demonstrated that no significant degradation occurs at hot junction temperatures of 900° to 1000°F in 2000 hours, the maximum time for which data are available. Post-test examination of life test samples showed the presence of extensive interdiffusion between the braze material and the thermoelectric element. This, however, appears to have no effect on performance. Such a result is expected for n-PbTe since poisoning effects studies carried out earlier in this program indicated that SnTe additions did not appreciably alter the properties of the n-type thermoelectric.

The process developed for bonding n-PbTe cannot be successfully applied to p-PbTe without modification. It was found that the stresses generated during the cooling cycle resulting from the thermal expansion mismatch between the element and shoe were sufficient to introduce cracks in the weak p-type material. Several additives were studied to see if they might strengthen p-PbTe without adversely affecting its thermoelectric properties. Molybdenum appears to be particularly promising. On the basis of preliminary results, the strength of p-PbTe can be increased to that of n-PbTe with only small changes in initial thermoelectric properties. A 500 hour life test of one sample yielded inconclusive results, i. e., power output declined approximately 10 percent but a similar drop was observed in a sample containing no additive. Detailed analyses will be performed to obtain a better understanding of the observed strengthening mechanism.

Life tests of n-PbTe and p-PbTe will be continued during the next quarter and further studies of additive effects on p-PbTe will be undertaken. Bonding process development for p-PbTe will continue.

VII. REFERENCES

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2. Thermoelectric Bonding Study - Quarterly Progress Report Covering the Period from 1 June through 31 August 1965. Report No. HIT-186 prepared under Contract NAS5-3973 (September 30, 1965).
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